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(54) Title: CATALYST COMPOSITION TO GET POLYURETHANE PRODUCT WITH GOOD HYDROLYSIS RESISTANCE

(57) Abstract: The present invention discloses catalyst compositions for producing polyurethane products having improved heat and humid aging properties and to processes for the manufacture of polyurethane products using such catalysts. The catalysts are based on a blend of at least one compound having a tertiary amine and isocyanate reactive group and at least one compound having a quaternary ammonium alkoxide moiety and at least one tertiary amine group wherein the later compound is partially or completely neutralized with at least one acidic compound.

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**CATALYST COMPOSITION TO GET POLYURETHANE PRODUCT WITH GOOD
HYDROLYSIS RESISTANCE**

The present invention pertains to catalyst compositions
5 giving polyurethane products with superior heat and humid aging
resistance, to processes for their manufacture and to polyurethane
products produced therefrom.

Polyether polyols based on the polymerization of
10 alkylene oxides, and/or polyester polyols, are the major components
of a polyurethane system together with isocyanates. Polyols can
also be filled polyols, such as SAN (Styrene/Acrylonitrile), PIPA
(polyisocyanate polyaddition) or PHD (polyurea) polyols, as
described in "Polyurethane Handbook", by G. Oertel, Hanser
15 publisher. These systems generally contain additional components
such as cross-linkers, chain extenders, surfactants, cell
regulators, stabilizers, antioxidants, flame retardant additives,
eventually fillers, and typically catalysts such as tertiary amines
and/or organometallic salts.

20 The organometallic catalysts used for making
polyurethanes, such as lead or mercury salts, can raise
environmental issues due to leaching upon aging of the polyurethane
products. Others, such as tin salts, are often detrimental to
25 polyurethane aging.

The commonly used, fugitive tertiary amine catalysts,
can also give rise to undesirable environmental issues,
particularly in flexible, semi-rigid and rigid foam applications.
30 Foams using these catalysts often exhibit the typical odor of the
amines and give rise to increased fogging (emission of volatile
products). On another hand, fugitive catalysts give polyurethane
products with superior heat and humid aging resistance as they
leave the polyurethane product, and thus do not catalyze retro-
35 reactions upon aging.

The presence, or formation, of even traces of tertiary
amine catalyst vapors in polyurethane products having vinyl films
or polycarbonate sheets exposed thereto can be disadvantageous.

Specifically, the tertiary amine catalysts present in polyurethane foams have been linked to the staining of the vinyl film and degradation of polycarbonate sheets. This PVC staining and polycarbonate decomposition problems are especially prevalent in environments wherein elevated temperatures may exist for long periods of time, such as in automobile interiors.

Various solutions to this problem have been proposed. One is the use of amine catalysts which contain a hydrogen isocyanate reactive group, that is a hydroxyl or a primary and/or a secondary amine. Such a compound is disclosed in EP 747,407. Other types of reactive monol catalysts are described in U.S. Patents 4,122,038, 4,368,278, 4,510,269 and 5,539,007. Since most of them are monofunctional, these reactive amines act as chain stoppers and have a detrimental effect on the polymer build up hence affect polyurethane product physical characteristics, such as humid and heat aging resistance. Other types of reactive amine catalysts are claimed in US 3,448,065, in EP 677,540, in EP 1,109,847 and in EP 1,262,500. A reported advantage of the reactive catalyst compositions is that they are incorporated into the polyurethane product. However those catalysts have to be used at high levels in the polyurethane formulation to compensate for their lack of mobility during the reactions.

Various other means have been proposed for incorporating a reactive amine into a polyol. Modification of conventional polyols by partial amination has been disclosed in U.S. Patent 3,838,076. Pre-polymerization of reactive amine catalysts with a polyisocyanate and a polyol is reported in PCT WO 94/02525. Use of specific amine-initiated polyols is proposed in EP 539,819, in U.S. Patent 5,672,636 and in WO 01/ 58,976. While these approaches can reduce the amount of amine catalyst required in the system, there are disadvantages associated with each process similar to reactive amines, that is leading to polyurethane products with poor resistance against heat and humid aging.

Modifications of polyether polyols along the length of the polyol chain with epoxy resin-diamine or epoxy resin -amino-alcohol adducts are described in U.S. Patents 4,518,720, 4,535,133

and 4,609,685. The addition of epoxy along the internal length of the polyol chain is reported to increase the overall functionality of the polyol chain. Flexible foam produced from such polyols reportedly have equivalent firmness and better elongation
5 properties than foams made with a similar molecular weight unmodified polyol. Polyepoxides containing at least one tertiary nitrogen as described in U.S. Patent 4,775,558 are reported to improve the thermal stability of polyurethane products in contact with a non-polyurethane foil. However, conventional fugitive
10 catalysts are used and there are no mention of humid aging characteristics.

Quaternary amine based catalyst compositions using epoxide chemistry are described in US 3,010,963, in US 3,892,687;
15 in US 3,993,652; in US 4,404,120 and in US 4,040,992. These are effective for isocyanate trimerization, an undesirable reaction in flexible foams, since it gives softer foam with poor heat and humid aging characteristics. Other quaternary ammonium compositions and uses are claimed in US 2,981,700; US 3,042,632; US 3,108,975; US
20 3,226,345; US 3,726,816; US 4,324,879. Use of alkali metal alkoxide is also described in US 5,147,898 to produce rigid foam.

Control of the isocyanate trimerization and/or urethane reactions by the use of various acidic compounds together with
25 quaternary ammonium or other compounds is described in US 4,324,879; US 4,503,226. Other catalyst deactivations using acidic compounds are claimed in US 3,621,020; US 3,969,288; US 4,120,884; US 4,738,991; US 4,837,321 US 5,373,028; US 5,719,229; US 2002/0153507.

30

None of above-referenced documents disclose improvement of humid aging characteristics of the polyurethane products made therefrom.

35

Therefore, there continues to be a need for development of reactive catalyst compositions so that the production of heat and humid aged stable polyurethane products can be obtained without the need for low molecular weight, fugitive, tertiary amines as catalysts. The catalyst compositions should be suitable for the

preparation of flexible, compact or cellular polyisocyanate polyaddition products and should be readily miscible with other synthesis components.

5 It is an object of the present invention to provide a catalyst composition based on a blend of at least one tertiary amine molecule containing an isocyanate reactive group and at least one compound containing at least one quaternary ammonium alkoxide moiety and at least one tertiary amine group, wherein the later
10 compound is partially or totally neutralized with at least one acidic compound. Such catalyst compositions are useful in the production of polyurethane products containing a reduced level of conventional, fugitive, tertiary amine catalysts, or production of such products in the absence of such amine catalysts. It is
15 another objective of the present invention to produce polyurethane products containing a reduced level of organometallic catalyst or to produce such products in the absence of organometallic catalysts. With the reduction of the amount of amine and/or
20 organometallic catalysts needed or elimination of such catalysts, the disadvantages associated with such catalysts can be minimized or avoided.

 It is another object of the invention to have a process to adjust reactivity, such as gelation rate, and processing of a
25 polyurethane system without having to rely on amine and/or organometallic catalysts.

 It is a further object of the present invention to provide a catalyst composition so that the industrial manufacturing
30 process of the polyurethane product using these catalyst compositions and the physical characteristics of the polyurethane products, especially heat and humid aging resistance, made therefrom are not adversely affected and may even be improved by the reduction in the amount of conventional or reactive amine
35 catalysts or in elimination of the amine catalyst, and/or by reduction or elimination of organometallic catalysts.

In a further aspect, the present invention is a process for the production of a polyurethane product by reaction of a mixture of

- (a) at least one organic polyisocyanate with
- 5 (b) at least one polyol in the presence of
- (c) a catalyst composition comprising a blend of
 - (c1) at least one tertiary amine molecule containing an isocyanate reactive group and
 - 10 (c2) at least one compound containing at least one quaternary ammonium alkoxide moiety and at least one tertiary amine group, wherein (c2) is partially or totally neutralized with at least one acidic compound (c3);
- (d) optionally in the presence of a blowing agent; and
- 15 (e) optionally additives or auxiliary agents known per se for the production of polyurethane foams, elastomers and/or coatings.

In another embodiment, the present invention is a process whereby catalyst composition (c) is based on a blend of
20 (c1) and (c2) wherein the composition contains a higher percentage of (c1) versus (c2).

In another embodiment, the present invention is a process whereby part, or the whole, of the compound (c2) exhibits
25 autocatalytic characteristics for the polyurethane reactions.

In another embodiment, the present invention is a process whereby part, or the whole, of the compound (c2) contains at least one isocyanate reactive group.

30 In another embodiment, the present invention is a process whereby part, or the whole, of acidic compound (c3) used to neutralize partially or totally compound (c2) does not fully react with isocyanate under polyurethane foaming conditions.

In another embodiment, the present invention is a process whereby the acidic compound (c3) is used at a level sufficient to neutralize partially or totally the quaternary ammonium moiety of compound (c2) leaving the tertiary amine free to catalyze the polyurethane reactions.

In another embodiment, the present invention is a process whereby the acidic compound (c3) is used at a level sufficient to neutralize totally the quaternary ammonium moiety of compound (c2) and partially the tertiary amines of (c2) and (c1) to get delayed catalytic activity.

In another embodiment, the present invention is a process whereby the acidic compound (c3) is a blend of at least two acidic compounds.

In another embodiment, the present invention is a process whereby tertiary amine molecule containing an isocyanate reactive group (c1) and compound (c2) are based on the reaction between at least one reactive tertiary amine and at least one epoxide and not more than four epoxide moieties.

In another embodiment, the present invention is a process whereby at least one tertiary amine molecule containing an isocyanate reactive group (c1) is a polymer.

In another embodiment, the present invention is a process whereby part, or the whole, of the compound (c2) is a polymer.

In another embodiment, the present invention is a process whereby catalyst (c) is used when at least 2 percent by weight of polyol (b) is an autocatalytic polyol (b1).

In another embodiment, the present invention is a process whereby a small amount of conventional catalyst, fugitive amine and/or metallic salt, is used with compound (c2) in presence or absence of autocatalytic polyol (b1).

5

In another embodiment, the present invention is a process whereby compound (c2) has specific blowing and/or gelling characteristics and is able to replace at least 10 percent of the conventional catalysts, more preferably 30 percent and most preferably at least 50 percent of a conventional amine catalyst.

10

In another embodiment, the present invention is a process whereby no conventional catalyst, fugitive amine or metallic salt, is used with compound (c2) in presence or absence of autocatalytic polyol (b1).

15

In a further embodiment, the present invention is a process as disclosed above whereby the polyol (b) contains a polyol-terminated prepolymer obtained by the reaction of an excess of autocatalytic polyol (b1) with a polyisocyanate.

20

The invention further provides for polyurethane products produced by any of the above processes.

25

The catalyst composition (c) as disclosed in the present invention accelerates the addition reaction of organic polyisocyanates with polyhydroxyl or polyamino compounds and the reaction between the isocyanate and the blowing agent such as water or a carboxylic acid or its salts. The addition of these catalyst compositions (c) to a polyurethane reaction mixture reduces or eliminates the need to include a conventional tertiary amine catalyst or an organometallic catalyst within the mixture. When these catalyst compositions (c) contain reactive hydrogens, they can react with the isocyanate and become part of the polymer. The reduction in use of a tertiary amine or organometallic catalysts reduces the disadvantages associated with such catalysts. Their

30

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addition to polyurethane reaction mixtures can also reduce the mold dwell time in the production of molded foams and improve key polyurethane product properties, such as resistance to heat and/or humid aging.

5

As used herein the term polyols are those materials having at least one group containing an active hydrogen atom capable of undergoing reaction with an isocyanate. Preferred among such compounds are materials having at least two hydroxyls, primary or secondary, or at least two amines, primary or secondary,
10 carboxylic acid, or thiol groups per molecule. Compounds having at least two hydroxyl groups or at least two amine groups per molecule are especially preferred due to their desirable reactivity with polyisocyanates. Autocatalytic polyols (b1), which can be a
15 component of (b), are polyols which have a hydroxyl number from 15 to 800 and catalyze the urethane reaction. Such polyols are generally made from amine initiators. See for example WO 01/58976 and U.S. Patents 5,476,969 and 5,672,636.

20

Suitable polyols (b) that can be used to produce polyurethane materials with the catalyst composition (c) of the present invention are well known in the art and include those described herein and any other commercially available polyol and/or SAN, PIPA or PHD copolymer polyols. Such polyols are described in
25 "Polyurethane Handbook", by G. Oertel, Hanser publishers. Mixtures of one or more polyols and/or one or more copolymer polyols may also be used to produce polyurethane products according to the present invention.

30

Representative polyols include polyether polyols, polyester polyols, polyhydroxy-terminated acetal resins, hydroxyl-terminated amines and polyamines. Examples of these and other suitable isocyanate-reactive materials are described more fully in U.S. Patent 4,394,491. Alternative polyols that may be used
35 include polyalkylene carbonate-based polyols and polyphosphate-based polyols. Preferred are polyols prepared by adding an alkylene oxide, such as ethylene oxide (EO), propylene oxide (PO), butylene oxide (BO) or a combination thereof, to an initiator having from 2 to 8, preferably 2 to 6 active hydrogen atoms.

Catalysis for this polymerization can be either anionic or cationic, with catalysts such as KOH, CsOH, boron trifluoride, or a double cyanide complex (DMC) catalyst such as zinc hexacyanocobaltate or quaternary phosphazanium compound. In the case of alkaline catalysts, these alkaline catalysts are preferably eliminated from the polyol at the end of production by a finishing step, such as coalescence, magsil (magnesium silicate) separation or acid neutralization.

The polyol or blends thereof employed depends upon the end use of the polyurethane product to be produced. The molecular weight or hydroxyl number of the base polyol may thus be selected so as to result in flexible, semi-flexible, integral-skin or rigid foams, elastomers or coatings, or adhesives when the polymer/polyol produced from the base polyol is converted to a polyurethane product by reaction with an isocyanate, and depending on the end product in the presence of a blowing agent. The hydroxyl number and molecular weight of the polyol or polyols employed can vary accordingly over a wide range. In general, the hydroxyl number of the polyols employed may range from 15 to 800.

In the production of a flexible polyurethane foam, the polyol is preferably a polyether polyol and/or a polyester polyol. The polyol generally has an average functionality ranging from 2 to 5, preferably 2 to 4, and an average hydroxyl number ranging from 20 to 100 mg KOH/g, preferably from 20 to 70 mgKOH/g. As a further refinement, the specific foam application will likewise influence the choice of base polyol. As an example, for molded foam, the hydroxyl number of the base polyol may be on the order of 20 to 60 with ethylene oxide (EO) capping, and for slabstock foams the hydroxyl number may be on the order of 25 to 75 and is either mixed feed EO/PO (propylene oxide) or is only slightly capped with EO or is 100 percent PO based. For elastomer applications, it will generally be desirable to utilize relatively high molecular weight base polyols, from 2,000 to 8,000, having relatively low hydroxyl numbers, for example, 20 to 50.

Typically polyols suitable for preparing rigid polyurethanes include those having an average molecular weight of

100 to 10,000 and preferably 200 to 7,000. Such polyols also advantageously have a functionality of at least 2, preferably 3, and up to 8, preferably up to 6, active hydrogen atoms per molecule. The polyols used for rigid foams generally have a
5 hydroxyl number of 200 to 1,200 and more preferably from 300 to 800.

For the production of semi-rigid foams, it is preferred to use a trifunctional polyol with a hydroxyl number of 30 to 80.

10

The initiators for the production of polyols (b) generally have 2 to 8 functional groups that will react with the alkylene oxide. Examples of suitable initiator molecules are water, organic dicarboxylic acids, such as succinic acid, adipic
15 acid, phthalic acid and terephthalic acid and polyhydric, in particular dihydric to octahydric alcohols or dialkylene glycols, for example ethanediol, 1,2- and 1,3-propanediol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol and sucrose
20 or blends thereof. Other initiators include compounds linear and cyclic amine compounds containing eventually a tertiary amine such as ethanoldiamine, triethanoldiamine, and various isomers of toluene diamine, ethylenediamine, N-methyl-1,2-ethanediamine, N-Methyl-1,3-propanediamine, N,N-dimethyl-1,3-diaminopropane, N,N-
25 dimethylethanolamine, 3,3'-diamino-N-methyldipropylamine, aminopropyl-imidazole, N,N-dimethyl-1,4-diaminobutane, N,N-dimethyldipropylenetriamine.

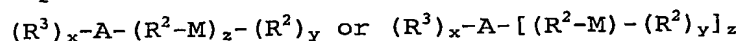
Amine based polyol (b1) can also contain a tertiary
30 nitrogen in the chain, by using for instance an alkyl-aziridine as co-monomer with PO and EO, or (b1) can be capped with this tertiary amine, by using for example a N,N-dialkyl-glycidylamine.

The catalysts (c) in the present invention are based
35 upon the reaction of an amine compound with an epoxide resin. Such amines include secondary amines and/or molecules which contain a tertiary amine and at least one reactive hydrogen able to react with an epoxide. Groups reactive with epoxides include primary or secondary, aliphatic or aromatic amines; primary, secondary and/or

tertiary alcohols; phenol; amides; ureas; and urethanes. It has been found that in the production of such catalysts, part of the tertiary amine present will react with an epoxide resin to give a quaternary ammonium alkoxide. As it is preferred to minimize the formation of (c2); the molar ratio of (c1) to (c2) is generally from 0.99 to 0.5; preferably the ratio is greater than 0.6. More preferably the ratio of (c1) to (c2) is greater than 0.7.

Generally, secondary amines can be represented by HNR_2^1 where each R^1 is independently a moiety having 1 to 20 carbon atoms, such as a linear or branched alkyl or alkylaryl, or may be attached together with the nitrogen atom and optionally other hetero atoms and alkyl-substituted hetero atoms to form one or two saturated unsaturated heterocyclic rings or aromatic ring(s).

Compounds containing at least one tertiary nitrogen and at least one hydrogen atom reactive to an epoxide can be represented by



where A is either hydrogen, nitrogen or oxygen;

x is 0, 1 or 2;

z is 1 or 2

with the provisos x is zero when A is hydrogen, x and z are 1 when A is oxygen, and when A is nitrogen x and z can be 1 or 2 with the sum of x and z being 3;

R^2 at each occurrence is independently a moiety having 1 to 20 carbon atoms;

R^3 is hydrogen or a moiety having 1 to 20 carbon atoms;

M is an amine or polyamine, linear, branched or cyclic, with at

least one tertiary amine group; and

y is an integer from 0 to 6. Other compounds which contain at least one tertiary nitrogen and at least one hydrogen atom reactive to an epoxide can be represented by the formula $(\text{H})_d\text{-Y-}(\text{R}^2\text{-M-}(\text{R}^2)_y)_b$ where M, R^2 and y are as previously defined, Y is oxygen or

nitrogen, b and d are 1 when Y is oxygen and when Y is nitrogen, b and d are either 1 or 2 such that the sum of b and d is 3.

Preferably M has a molecular weight of 30 to 300. More preferably M has a molecular weight of 50 to 200.

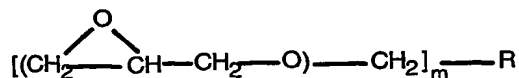
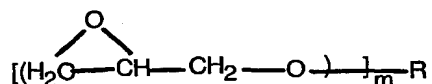
Examples of amines that are commercially available and that can be used to manufacture catalyst composition (c) are dimethylamine, diethylamine, N,N-dimethylethanolamine, N,N-dimethyl-N'-ethylenediamine, 3-dimethylamino-1-propanol, 1-
5 dimethylamino-2-propanol, 3-(dimethylamino) propylamine, dicyclohexylamine, 1-(3-aminopropyl)-imidazole, 3-hydroxymethyl quinuclidine, imidazole, 2-methyl imidazole, 1-(2-aminoethyl)-piperazine, 1-methyl-piperazine, 3-quinuclidinol, tetramethylamino-bis-propylamine, 2-(2-aminoethoxy)-ethanol, N,N-dimethylaminoethyl-
10 N'-methyl ethanolamine and 2-(methylamino)-ethanol, 1-methylpiperazine. Other types of amines which can be used with the present invention are N,N'-dimethylethylenediamine, 4,6-dihydroxypyrimidine, 2,4-diamino-6-hydroxypyrimidine, 2,4-diamino-6-methyl-1,3,5-triazine, 3-aminopyridine, 2,4-diaminopyrimidine, 2-
15 phenyl-imino-3-(2-hydroxyethyl)-oxazalodine, N-(2-hydroxyethyl)-2-methyl-tetrahydropyrimidine, N-(2-hydroxyethyl)-imidazoline, 2,4-bis-(N-methyl-2-hydroxyethylamino)-6-phenyl-1,3,5-triazine, bis-(dimethylaminopropyl)amino-2-propanol, 2-(2-methylaminoethyl)-pyridine, 2-(methylamino)-pyridine, 2-methylaminomethyl-1,3-
20 dioxane, and dimethylaminopropyl urea and blends thereof.

Amines used in the present invention can also be polymers, such as amine capped polyols or polyamines. In that case monomeric epoxy compounds are preferred.

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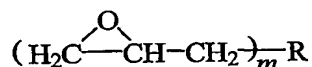
Standard epoxides can be used for producing the catalyst composition (c). See for example, U.S. Patent 4,609,685. The epoxide materials can be monomeric, such as ethylene oxide, propylene oxide or butylene oxide, or polymeric, saturated or
30 unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted if desired with other substituents besides the epoxy groups, for example, hydroxyl, ether radicals and aromatic halogen atoms. Preferred epoxides are aliphatic or cycloaliphatic polyepoxides, or glycidyl ethers, more preferably
35 diepoxides or triepoxides.

Particularly useful polyepoxide compounds which can be used in the practice of the present invention are polyepoxides having the following general formula:



5

or



wherein R is substituted or unsubstituted aromatic, aliphatic,
 10 cycloaliphatic or heterocyclic polyvalent group and m is an integer from 1
 up to the valence of R. Preferably m does not exceed 3 and preferably m
 is 1 or 2.

Examples of common epoxy resins include for example, the
 15 diglycidyl ethers of resorcinol, catechol, hydroquinone, bisphenol,
 bisphenol A, bisphenol AP (1,1-bis(4-hydroxylphenyl)-1-phenyl
 ethane), bisphenol F, bisphenol K, tetrabromobisphenol A, phenol-
 formaldehyde novolac resins, alkyl substituted phenol-formaldehyde
 resins, phenol-hydroxybenzaldehyde resins, cresol-
 20 hydroxybenzaldehyde resins, dicyclopentadiene-phenol resins,
 trimethylolpropane triglycidyl ether, dicyclopentadiene-substituted
 phenol resins tetramethylbiphenol, tetramethyl-tetrabromobiphenol,
 tetramethyltribromobiphenol, tetrachlorobisphenol A and any
 combination thereof.

25

Examples of preferred diepoxides are hydrogenated liquid
 aromatic epoxy resins of bis-phenol A or bisphenol F; and
 diepoxides D.E.R. 736, D.E.R. 732 (aliphatic epoxides) and ERL-4221
 (cyclic aliphatic epoxide) available from The Dow Chemical Company.

A mixture of any two or more polyepoxides can be used in the practice of the present invention. Preferably the epoxide resin has an average equivalent weight of 90 to 500. More preferably the epoxy resin has an average equivalent weight of 150 to 400.

5

Polyepoxides can be prepared by epoxidizing the corresponding allyl ethers or reacting a molar excess of epichlorohydrin and an aromatic polyhydroxy compound, such as novolak, isopropylidene bisphenol, resorcinol, etc. Polyepoxides
10 can also be obtained by reacting an epichlorohydrin with either a polyhydric phenol or a polyhydric alcohol.

Usually epoxide resins contain a relatively high amount of chlorine, both under the form of chloromethyl groups and as
15 ionic chloride. For instance D.E.R. 736, an epoxide resin available from The Dow Chemical Company, has about 10 percent total chlorine. Of particular interest for the present invention are low chlorine epoxy resins with less than 5 percent and more preferably less than 1 percent total chlorine.

20

Preferred catalyst compositions (c) are epoxides reacted with an amine based compound as described above. When using a polyepoxide resin it is preferred to have at least 70 percent of these epoxide groups reacted with the amine, more preferably 90
25 percent and most preferably 100 percent. More than one amine or aminoalcohols can be reacted with the epoxide resins.

The production of catalyst composition (c) is based on the reactions of at least one epoxide with at least one amine based
30 molecule to obtain a tertiary amine function in the final polymer molecule. The two or more reactants can be mixed together or the epoxide can first be pre-reacted partially with the amine(s) before further addition or vice versa the amine(s) can be in excess at the beginning of the reaction. Stoichiometric ratio between the amine
35 and the epoxy resin can be used, or preferably excess of one of the components may be favored to adjust final product characteristics. Addition of heat or cooling and proper catalysis may be used to control these reactions. Additionally other compounds can be used to help producing these amine epoxy adducts, that is co-reactants,

solvents etc. It is important to note that these epoxide-reactive hydrogen reactions generate hydroxyl groups.

Acidic compounds (c3) used to partially or totally
5 neutralize (c1) and/or (c2) are those able to neutralize an alkoxide, these are organic or inorganic acids, esters or polyesters, organic halogen based compounds with a labile halogen atom, aromatic mono-halide compounds containing at least one
10 electron-withdrawing nitro group ortho or para to the halogen, epoxy resins with high levels of halogen. Preferred acidic compounds to manufacture catalyst compositions (c) are those which have conjugate bases with low reactivity to isocyanates.

Examples of commercially available acidic compounds (c3)
15 are hydrochloric, phosphoric, tetrafluoric, dodecylbenzenesulfonic, chloroacetic, lactic, formic, 2-ethylhexanoic, ricinoleic acid, acetic anhydride, benzyl chloride, benzoyl chloride, toluoyl chloride, ethylene chloroacetate, alpha chlorodimethyl sulfoxide, tosylates, mesylates, and 4-nitro benzoyl chloride. Compounds
20 containing a hydrolysable chloride, such as epoxy resins D.E.R. 732, D.E.R. 736 available from The Dow Chemical Company, can be used. Blends of the acidic compounds may also be used.

The properties of catalyst compositions (c) can vary
25 widely and such parameters as average molecular weight, hydroxyl number, functionality, etc. will generally be selected based on the end use application of the formulation, that is, what type of polyurethane product to be produced.

30 The limitations described with respect to the characteristics of catalyst compositions (c) above are not intended to be restrictive but are merely illustrative of the large number of possible combinations for the epoxides, the amines and the acidic compounds used.

35 In a preferred embodiment the epoxide of catalyst compositions (c) is a diepoxide and the amine based molecule containing at least one reactive hydrogen has a methyl-amino or a dimethyl amino or an amidine or a pyridine or a pyrimidine or a

quinuclidine or an adamantane or a triazine or an imidazole or a piperazine structure combined with secondary and/or primary amines and/or secondary and/or primary hydroxyls.

5 The weight ratio of (c1) to (c2) and the level of (c3) will vary depending on the amount of additional catalyst one may desire to add to the reaction mix and to the reaction profile required by the specific application. Generally if a reaction mixture with a base level of fugitive catalyst having specified
10 curing time, (c) is added in an amount so that the curing time is equivalent where the reaction mix contains at least 10 percent by weight less catalyst. Preferably the addition of (c) is added to give a reaction mixture containing 20 percent less catalyst than the base level. More preferably the addition of (c) will reduce
15 the amount of catalyst required by 30 percent over the base level. For some applications, the most preferred level of (c) addition is where the need for a fugitive or reactive tertiary amine catalysts or organometallic salt is eliminated. Generally the amount of fusible catalyst is used in an amount from 1 to 10 percent by
20 weight of the polyol component (b).

Combination of two or more catalyst compositions of (c) type can also be used with satisfactory results in a single polyurethane formulation when one wants for instance to adjust
25 blowing and gelling reactions modifying the epoxide and/or the amine structures with different tertiary amines, functionalities, equivalent weights, etc, and their respective amounts in the formulations, as well as the type and level of acidic compounds (c3).

30 The isocyanates which may be used with the catalyst compositions (c) of the present invention include aliphatic, cycloaliphatic, arylaliphatic and aromatic isocyanates. Aromatic isocyanates, especially aromatic polyisocyanates are preferred.

35 Examples of suitable aromatic isocyanates include the 4,4'-, 2,4' and 2,2'-isomers of diphenylmethane diisocyanate (MDI), blends thereof and polymeric and monomeric MDI blends toluene-2,4- and 2,6-diisocyanates (TDI), m- and p-phenylenediisocyanate,

chlorophenylene-2,4-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate-3,3'-dimehtyldiphenyl, 3-methyldiphenyl-methane-4,4'-diisocyanate and diphenyletherdiisocyanate and 2,4,6-triisocyanatotoluene and 2,4,4'-triisocyanatodiphenylether.

5

Mixtures of isocyanates may be used, such as the commercially available mixtures of 2,4- and 2,6-isomers of toluene diisocyanates. A crude polyisocyanate may also be used in the practice of this invention, such as crude toluene diisocyanate
10 obtained by the phosgenation of a mixture of toluene diamine or the crude diphenylmethane diisocyanate obtained by the phosgenation of crude methylene diphenylamine. TDI/MDI blends may also be used. MDI or TDI based prepolymers can also be used, made either with polyol (b1), or any other polyol as described heretofore.
15 Isocyanate-terminated prepolymers are prepared by reacting an excess of polyisocyanate with polyols, including aminated polyols or imines/enamines thereof, or polyamines.

Examples of aliphatic polyisocyanates include ethylene
20 diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane 1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, saturated analogues of the above mentioned aromatic isocyanates and mixtures thereof.

25 The preferred polyisocyanates for the production of rigid or semi-rigid foams are polymethylene polyphenylene isocyanates, the 2,2', 2,4' and 4,4' isomers of diphenylmethylene diisocyanate and mixtures thereof. For the production of flexible foams, the preferred polyisocyanates are the toluene-2,4- and 2,6-
30 diisocyanates or MDI or combinations of TDI/MDI or prepolymers made therefrom.

For rigid foam, the organic polyisocyanates and the isocyanate reactive compounds are reacted in such amounts that the
35 isocyanate index, defined as the number or equivalents of NCO groups divided by the total number of isocyanate reactive hydrogen atom equivalents multiplied by 100, ranges from 80 to less than 500 preferably from 90 to 100 in the case of polyurethane foams, and from 100 to 300 in the case of combination polyurethane-

polyisocyanurate foams. For flexible foams, this isocyanate index is generally between 50 and 120 and preferably between 75 and 110.

For elastomers, coating and adhesives the isocyanate index is generally between 80 and 125, preferably between 100 to 110.

For producing a polyurethane-based foam, a blowing agent is generally required. In the production of flexible polyurethane foams, water is preferred as a blowing agent. The amount of water is preferably in the range of from 0.5 to 10 parts by weight, more preferably from 2 to 7 parts by weight based on 100 parts by weight of the polyol. Carboxylic acids or salts are also used as reactive blowing agents. Other blowing agents can be liquid or gaseous carbon dioxide, methylene chloride, acetone, pentane, isopentane, methylal or dimethoxymethane, dimethylcarbonate. Use of artificially reduced or increased atmospheric pressure can also be contemplated with the present invention.

In the production of rigid polyurethane foams, the blowing agent includes water, and mixtures of water with a hydrocarbon, or a fully or partially halogenated aliphatic hydrocarbon. The amount of water is preferably in the range of from 2 to 15 parts by weight, more preferably from 2 to 10 parts by weight based on 100 parts of the polyol. With excessive amount of water, the curing rate becomes lower, the blowing process range becomes narrower, the foam density becomes lower, or the moldability becomes worse. The amount of hydrocarbon, the hydrochlorofluorocarbon, or the hydrofluorocarbon to be combined with the water is suitably selected depending on the desired density of the foam, and is preferably not more than 40 parts by weight, more preferably not more than 30 parts by weight based on 100 parts by weight of the polyol. When water is present as an additional blowing agent, it is generally present in an amount from 0.5 to 10, preferably from 0.8 to 6 and more preferably from 1 to 4 and most preferably from 1 to 3 parts by total weight of the total polyol composition.

Hydrocarbon blowing agents are volatile C₁ to C₅ hydrocarbons. The use of hydrocarbons is known in the art as disclosed in EP 421 269 and EP 695 322. Preferred hydrocarbon blowing agents are butane and isomers thereof, pentane and isomers thereof (including cyclopentane), and combinations thereof.

Examples of fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane, 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoroethane (HFC-134a), pentafluoroethane, difluoromethane, perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane, pentafluorobutane (HFC-365mfc), heptafluoropropane and pentafluoropropane.

Partially halogenated chlorocarbons and chlorofluorocarbons for use in this invention include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-trichloroethane, 1,1-dichloro-1-fluoroethane (FCFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142b), 1,1-dichloro-2,2,2-trifluoroethane (HCHC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124).

Fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11) dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), 1,1,1-trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane. The halocarbon blowing agents may be used in conjunction with low-boiling hydrocarbons such as butane, pentane (including the isomers thereof), hexane, or cyclohexane or with water.

In addition to the foregoing critical components, it is often desirable to employ certain other ingredients in preparing polyurethane polymers. Among these additional ingredients are surfactants, preservatives, flame retardants, colorants, antioxidants, reinforcing agents, stabilizers and fillers, including recycled, powdered polyurethane foam.

In making polyurethane foam, it is generally preferred to employ an amount of a surfactant to stabilize the foaming reaction mixture until it cures. Such surfactants advantageously comprise a liquid or solid organosilicone surfactant. Other
5 surfactants include polyethylene glycol ethers of long-chain alcohols, tertiary amine or alkanolamine salts of long-chain alkyl acid sulfate esters, alkyl sulfonic esters and alkyl arylsulfonic acids. Such surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and the
10 formation of large, uneven cells. Typically, 0.2 to 3 parts of the surfactant per 100 parts by weight total polyol (b) are sufficient for this purpose.

One or more catalysts for the reaction of the polyol
15 (and water, if present) with the polyisocyanate can be used. Any suitable urethane catalyst may be used, including tertiary amine compounds, amines with isocyanate reactive groups and organometallic compounds. Preferably the reaction is carried out in the absence of a fugitive amine or an organometallic catalyst or
20 a reduced amount as described above. Exemplary tertiary amine compounds include triethylenediamine, N-methylmorpholine, N,N-dimethylcyclohexylamine, pentamethyldiethylenetriamine, tetramethylethylenediamine, bis (dimethylaminoethyl)ether, 1-methyl-4-dimethylaminoethyl-piperazine, 3-methoxy-N-
25 dimethylpropylamine, N-ethylmorpholine, dimethylethanolamine, N-cocomorpholine, N,N-dimethyl-N',N'-dimethyl isopropylpropylenediamine, N,N-diethyl-3-diethylamino- propylamine and dimethylbenzylamine. Exemplary organometallic catalysts include organomercury, organolead, organoferric and organotin
30 catalysts, with organotin catalysts being preferred among these. Suitable tin catalysts include stannous chloride, tin salts of carboxylic acids such as dibutyltin di-laurate, as well as other organometallic compounds such as are disclosed in U.S. Patent 2,846,408, or in EP 1,013,704, EP 1,167,410, EP 1,167,411. A
35 catalyst for the trimerization of polyisocyanates, resulting in a polyisocyanurate, such as an alkali metal alkoxide, may also optionally be employed herein, especially for rigid foams. The amount of amine catalysts can vary from 0.02 to 5 percent in the

formulation or organometallic catalysts from 0.001 to 1 percent in the formulation can be used.

A crosslinking agent or a chain extender may be added, if necessary. The crosslinking agent or the chain extender includes low-molecular polyhydric alcohols such as ethylene glycol, diethylene glycol, 1,4-butanediol, and glycerin; low-molecular amine polyol such as diethanolamine and triethanolamine; polyamines such as ethylene diamine, xylenediamine, and methylene-bis(o-chloroaniline). The use of such crosslinking agents or chain extenders is known in the art as disclosed in U.S. Patents 4,863,979 and 4,963,399 and EP 549,120.

When preparing rigid foams for use in construction, a flame retardant is generally included as an additive. Any known liquid or solid flame retardant can be used with the autocatalytic polyols of the present invention. Generally such flame retardant agents are halogen-substituted phosphates and inorganic flame proofing agents. Common halogen-substituted phosphates are tricresyl phosphate, tris(1,3-dichloropropyl phosphate, tris(2,3-dibromopropyl) phosphate and tetrakis (2-chloroethyl)ethylene diphosphate. Inorganic flame retardants include red phosphorous, aluminum oxide hydrate, antimony trioxide, ammonium sulfate, expandable graphite, urea or melamine cyanurate or mixtures of at least two flame retardants. In general, when present, flame retardants are added at a level of from 5 to 50 parts by weight, preferable from 5 to 25 parts by weight of the flame retardant per 100 parts per weight of the total polyol present.

The applications for foams produced by the present invention are those known in the industry. For example rigid foams are used in the construction industry and for insulation for appliances and refrigerators. Flexible foams and elastomers find use in applications such as furniture, mattresses, shoe soles, automobile seats, sun visors, steering wheels, armrests, door panels, noise insulation parts and dashboards.

Processing for producing polyurethane products are well known in the art. In general components of the polyurethane-

forming reaction mixture may be mixed together in any convenient manner, for example by using any of the mixing equipment described in the prior art for the purpose such as described in "Polyurethane Handbook", by G. Oertel, Hanser publisher.

5

The polyurethane products are either produced continuously or discontinuously, by injection, pouring, spraying, casting, calendering, etc; these are made under free rise or molded conditions, with or without release agents, in-mold coating, or any
10 inserts or skin put in the mold. In case of flexible foams, those can be mono- or dual-hardness.

For producing rigid foams, the known one-shot prepolymer or semi-prepolymer techniques may be used together with
15 conventional mixing methods including impingement mixing. The rigid foam may also be produced in the form of slabstock, moldings, cavity filling, sprayed foam, frothed foam or laminates with other material such as paper, metal, plastics or wood-board. Flexible foams are either free rise and molded while microcellular
20 elastomers are usually molded.

The following examples are given to illustrate the invention and should not be interpreted as limiting in anyway. Unless stated otherwise, all parts and percentages are given by
25 weight.

A description of the raw materials used in the examples is as follows.

30	DEOA 85 percent	is 85 percent pure diethanolamine and 15 percent water.
	2-Methylimidazole	is a tertiary amine with a reactive hydrogen available from Aldrich.
	Imidazole	is a tertiary amine with a reactive hydrogen available from Aldrich.
35	1-Methylpiperazine	is a tertiary amine with a reactive hydrogen available from Aldrich.
	D.E.R. 732	is an aliphatic diepoxide resin with an EEW (epoxy equivalent weight) of

325 available from The Dow Chemical Company.

5 Epoxide resin A is an aliphatic diepoxide resin with an EEW (epoxy equivalent weight) of 291 and containing less than 1 percent chloride.

 Dabco DC 5169 is a silicone-based surfactant available from Air Products and Chemicals Inc.

10 Dabco 33 LV is a tertiary amine catalyst available from Air Products and Chemicals Inc.

 Niaux A-1 is a tertiary amine catalyst available from Crompton Corporation.

15 Polyol B is a 1,700 equivalent weight propoxylated tetrol initiated with 3,3'-diamino-N-methyl dipropylamine and capped with 15 percent ethylene oxide.

20 SPECFLEX NC 632 is a 1,700 EW polyoxypropylene polyoxyethylene polyol initiated with a blend of glycerol and sorbitol available from The Dow Chemical Company.

 SPECFLEX NC-700 is a 40 percent SAN based copolymer polyol with an average hydroxyl number of 20 available from The Dow Chemical Company.

25 VORANATE T-80 is TDI 80/20 isocyanate available from The Dow Chemical Company.

30

 All foams were made in the laboratory with an Admiral high pressure machine equipped with Krauss-Maffei MK-12/16-UL-4K mix-head and by preblending polyols, surfactants, crosslinkers, catalysts and water. The reactants are poured in a 40x40x10 cm aluminum mold heated at 60°C which is subsequently closed. The mold had previously been sprayed with the release agent Klueber 41-2013 available from Klueber Chemie. Curing at 4 minutes is assessed by manually demolding the part and looking for defects.

Foam properties are measured according to ASTM D3574-95 test method for density (kg/m³) and Humid Aged Compression sets (HACS), that is compression set after 5 hours aging at 120°C and 100 percent Relative Humidity, and test method VW-AUDI PV 3410-93 for Tensile Strength (Kpa) and Elongation at Break (percent) after Humid Aging, that is 8 days at 90°C and 100 percent Relative Humidity.

10 Comparative Example A

A 1 L flask was charged with 100.3 grams (1.22 mole) of 2-methylimidazole, and 232.2 grams (0.798 mole epoxide groups) of epoxide resin A. The flask was fitted with an addition funnel containing an additional 230.3 grams (0.791 mole epoxide groups) of epoxide resin A and placed under an atmosphere of nitrogen. The flask was placed in a heating bath at 60°C. The internal temperature was controlled at 60°C by applying heating or cooling as necessary. After 3 hours of reaction time, the contents of the addition funnel were added dropwise over the course of 1 hour. After all the epoxy had been added, the reaction mixture was stirred at 60°C for an additional 3 hours. Diethylene glycol (140.1 g) was then added to the reaction mixture. The red/brown syrup was then poured out of the flask to yield 682 g of product. The product contains 1.74 mmol/g of 2-methylimidazole derived species. Product with substitution on the 1-position of 2-methylimidazole account for 82 mole percent of products, products with 1,3-disubstitution of 2-methylimidazole account for 18 mole percent of products.

30 Example 1

A one liter flask was charged with 100 grams (1.218 mole) of 2-methylimidazole and 264.5 grams (0.814 mole epoxide groups) of D.E.R. 732. The flask was fitted with an addition funnel containing an additional 250 grams (0.770 mole epoxy groups) of D.E.R. 732 and placed under an atmosphere of nitrogen. The flask was placed in a heating bath at 60°C. The internal temperature was controlled at 60°C by applying heating or cooling

as necessary. After 3 hours of reaction time, the contents of the addition funnel were added dropwise over the course of 4 hours. The highest observed temperature during the reaction was 78°C. After all the D.E.R. had been added, the reaction mixture was
5 stirred at 60°C overnight. A light yellow syrup, 603.7 grams was obtained. The product contains 1.988 mmol/g of 2-methylimidazole derived species. The level of ionic chloride in the sample is 43,000 ppm.

10 Example 2.

A 1 L flask was charged with 100.1 grams (1.22 mole) of 2-methylimidazole, and 231.1 grams (0.794 mole epoxide groups) of epoxide resin A. The flask was fitted with an addition funnel
15 containing an additional 230.2 grams (0.791 mole epoxide groups) of epoxide resin A and placed under an atmosphere of nitrogen. The flask was placed in a heating bath at 60°C. The internal temperature was controlled at 60°C by applying heating or cooling as necessary. After 3 hours of reaction time, the contents of the
20 addition funnel were added dropwise over the course of 1 hours. After all the epoxy had been added, the reaction mixture was stirred at 60°C an additional 4 hours. Diethylene glycol (DEG) (141 g) was then added to the reaction mixture. Products with substitution on the 1-position of 2-methylimidazole account for 84
25 mole percent of products, products with 1,3-disubstitution of 2-methylimidazole account for 16 mole percent of products. To neutralize the imidazolium alkoxide, 28.8 grams (0.20 mole) of 2-ethylhexanoic acid (EHA) was added to the reaction mixture. The clear red/brown syrup was then poured out of the flask into
30 bottles. to neutralize the imidazolium alkoxide The product contains 1.67 mmol/g of 2-methylimidazole derived species.

Example 3

The procedure of Example 2 was followed except that the
35 imidazolium salt was neutralized with 20.2 grams of concentrated hydrochloric acid (0.205 mole). The product contains 1.69 mmol/g of 2-methylimidazole derived species with 84 mole percent

substituted on the 1-position and 16 mole percent disubstituted on the 1 and 3 positions.

Example 4

5 The procedure of example 2 was followed except that the imidazolium salt was neutralized with 87.9 grams of dodecyl benzene sulfonic acid (DBSA) (0.27 mole). The product contains 1.54 mmol /g of 2-methylimidazole derived species with 78 mole percent substituted on the 1-position and 22 mole percent disubstituted on the 1 and 3 positions.

Example 5

15 The procedure of example 2 was followed except that the imidazolium salt was neutralized with 44.4 grams of 48 weight percent aqueous tetrafluoroboric acid (HBF₄) (0.2 mole). The product contains 1.62 mmol/g of 2-methylimidazole derived species with 81 mole percent substituted on the 1-position and 19 mole percent disubstituted on the 1 and 3 positions.

20 Example 6

 The procedure of example 2 was followed except that the imidazolium salt was neutralized with 1.25 mole equivalent or meq (based on the alkoxide) of a 85 percent aqueous solution of lactic acid, a hydroxy functional carboxylic acid.

25

Example 7

 The procedure of example 2 was followed except that the imidazolium salt was neutralized with 1.1 meq (based on the alkoxide) of chloroacetic acid.

30

Example 8

 The procedure of example 2 was followed except that the imidazolium salt was neutralized with 1.1 meq (based on the alkoxide) of toluoyl chloride.

35

Example 9

 The procedure of example 2 was followed except that a 50/50 mole ratio between 2-methylimidazole and imidazole was used together with 19.6 percent by weight of DEG and this adduct was

neutralized with 1.1 meq (based on the alkoxide) of hydrochloric acid (HCl).

Example 10

5 The procedure of example 2 was followed except that the imidazolium was neutralized with a blend of 0.6 meq of HCl and 0.6 meq of 2-EHA (based on the alkoxide).

Example 11

10 The procedure of example 2 was followed except that 1-methylpiperazine is used instead of 2-methylimidazole, and 2-EHA is the acid.

Example 12

15 The same procedure as example 11 is used except that the acid is HCl.

Example 13

20 The same procedure as example 11 is used except that the acid is DBSA.

Example 14

25 The same procedure as example 2 is used except 2-EHA is used at a level of 2 meq based on the alkoxide.

Examples 15 to 28

Foam properties, after aging, obtained with the following formulation, are reported in Table 1 below:

30	Specflex NC-632	18.5
	Adduct of examples 2 to 14	1.5
	Adduct of example 1	2.0
	Specflex NC-700	30
	Polyol B	50
35	Water	3.5
	DEOA 85 percent	0.8
	Dabco DC-5169	0.6
	Voramate T-80 (index)	100

Table 1

Adduct	Foam density	50 percent HACS (percent)	75 percent HACS (percent)	Tensile Strength	Elongation At break
Compara.					
Example A	35.9	62.9	80.5	13	34
Example 1	36.7	18.3	15.8	126	159
Example 2	36.1	43.1	61.5	18	40
Example 3	35.3	27.2	27.4	71	103
Example 4	37	21.3	18	74	124
Example 5	37	19.9	16.7	79	120
Example 6	37.1	62.4	67.2	22	50
Example 7	38.5	18.2	16.6	85	138
Example 8	36	16.9	18.8	84	137
Example 9	37.2	26.2	20.8	31	70
Example 10	39.7	21.3	16.6	25	49
Example 11	35.1	48.7	48.8	24	50
Example 12	36.7	32.1	30.3	26	55
Example 13	36.7	27	23.3	20	46
Example 14	39.3	30.5	30.1	13	34

5

Data of table 1 show very poor aging resistance (high HACS and low tensile strength and elongation at break) of foam made with un-neutralized adduct of comparative example 1. Positive effect of acid neutralization is clear from all HACS values of adducts from examples 1 through 14. A comparison between adducts of example 2 and example 14 shows that increasing the level of 2-EHA improved HACS. Best results are obtained with acidic compounds bearing a conjugate base with low reactivity with isocyanate under foaming conditions as shown from values of tensile strength and elongation at break obtained with adducts of example 3 (HCl), adduct of example 4 (DBSA), adduct of example 5 (HBF₄), adduct of example 7 (chloroacetic acid), adduct of example 8 (toluoyl

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15

chloride). Conventional carboxylic acids gave poorer tensile and elongation properties after humid aging.

5 Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

10

Claims:

1. A process for the production of a polyurethane product by reaction of a mixture of

5 (a) at least one organic polyisocyanate with

(b) at least one polyol

in the presence of

(c) a catalyst composition comprising a blend of

10 (c1) at least one tertiary amine molecule containing an isocyanate reactive group and

(c2) at least one compound containing at least one quaternary ammonium alkoxide moiety and at least one tertiary amine group, wherein (c2) is partially or totally neutralized with at least one acidic compound

15 (c3);

(d) optionally in the presence of a blowing agent; and

(e) optionally additives or auxiliary agents known per se for the production of polyurethane foams, elastomers and/or coatings.

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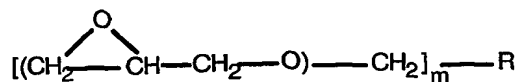
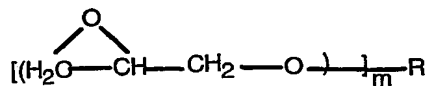
2. The process of Claim 1 wherein the catalyst is the reaction product of an amine with an epoxide.

25 3. The process of Claim 2 wherein the epoxide is an aliphatic or cycloaliphatic polyepoxide or glycidyl ether.

4. The process of Claim 3 wherein the polyepoxide is a diepoxide or triepoxide.

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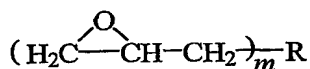
5. The process of Claim 2 wherein the epoxide is represented by one of the formulae



or

5

10



wherein R is substituted or unsubstituted aromatic, aliphatic, cycloaliphatic or heterocyclic polyvalent group and n had an average value of from 1 to less than 8 and m is an integer from 1 up to the valence of R.

6. The process of Claim 1 wherein the acid is selected from one or more of organic or inorganic acids, esters or polyesters, organic halogen based compounds with a labile halogen atom, aromatic mono-halide compounds containing at least one electron-withdrawing nitro group ortho or para to the halogen, or epoxy resins with high levels of halogen.

7. The process of Claim 6 wherein the acid is added in less than a stoichiometric amount to neutralize the quaternary amine in (c2).

8. The process of Claim 2 wherein the amine is represented by the formula $\text{HN}(\text{R}^1)_2$ where each R^1 is independently a compound having 1 to 20 carbon atoms or may be attached together with the nitrogen atom and optionally other hetero atoms and alkyl-

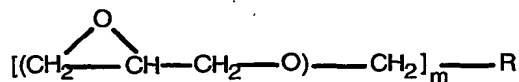
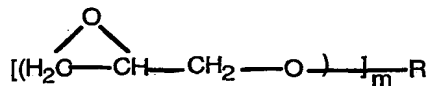
substituted hetero atoms to form a saturated or unsaturated heterocyclic ring.

9. The process of Claim 2 wherein the amine is
5 represented by the formula $(R^3)_x-A-(R^2-M)_z-(R^2)_y$ or $(R^3)_x-A-[(R^2-M)-(R^2)_y]_z$
where A is either hydrogen, nitrogen or oxygen;
x is 0, 1 or 2;
z is 1 or 2
10 with the provisos x is zero when A is hydrogen, x and z are 1 when A is oxygen, and when A is nitrogen x and z can be 1 or 2 with the sum of x and z being 3;
 R^2 at each occurrence is independently a moiety having 1 to 20 carbon atoms;
15 R^3 is hydrogen or a moiety having 1 to 20 carbon atoms;
M is an amine or polyamine, linear, branched or cyclic, with at least one tertiary amine group; and
y is an integer from 0 to 6.

- 20 10. The process of Claim 2 wherein the amine is represented by the formula $(H)_d-Y-(R^2-M-(R^2)_y)_b$ where
Y is oxygen or nitrogen;
 R^2 at each occurrence is independently a moiety having 1 to 20 carbon atoms;
25 M is an amine or polyamine, linear, branched or cyclic, with at least one tertiary amine group;
y is an integer from 0 to 6; and
b and d are 1 when Y is oxygen and when Y is nitrogen, b and d are either 1 or 2 such that the sum of b and d is 3.

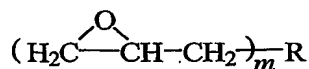
- 30 11. A polyurethane product produced by the process of anyone of Claims 1 to 10.

12. A polyurethane catalyst comprising the reaction
35 product of amine with an epoxide wherein the epoxide is selected from one or more compounds of the formulae



or

5



wherein R is substituted or unsubstituted aromatic, aliphatic, cycloaliphatic or heterocyclic polyvalent group and n had an average value of from 1 to less than 8 and m is an integer from 1 up to the valence of R;

and the amine is selected from one or more compounds of the formulae

$\text{HN}(\text{R}^1)_2$ wherein each R^1 is independently a compound having 1 to 20 carbon atoms or may be attached together with the nitrogen atom and optionally other hetero atoms and alkyl-substituted hetero atoms to form a saturated or unsaturated heterocyclic ring,

$(\text{R}^3)_x-\text{A}-(\text{R}^2-\text{M})_z-(\text{R}^2)_y$ or $(\text{R}^3)_x-\text{A}-[(\text{R}^2-\text{M})-(\text{R}^2)_y]_z$ where A is either hydrogen, nitrogen or oxygen;

x is 0, 1 or 2;

z is 1 or 2

with the provisos x is zero when A is hydrogen, x and z are 1 when A is oxygen, and when A is nitrogen x and z can be 1 or 2 with the sum of x and z being 3;

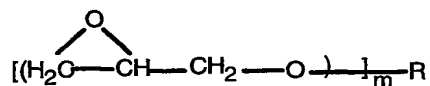
R^2 at each occurrence is independently a moiety having 1 to 20 carbon atoms;

R^3 is hydrogen or a moiety having 1 to 20 carbon atoms;

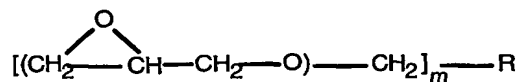
M is an amine or polyamine, linear, branched or cyclic, with at least one tertiary amine group; and

y is an integer from 0 to 6.

13. A polyurethane catalyst comprising the reaction product of amine with an epoxide wherein the epoxide is selected from one or more compounds of the formulae

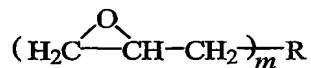


5



or

10



wherein R is substituted or unsubstituted aromatic, aliphatic, cycloaliphatic or heterocyclic polyvalent group and n had an average value of from 1 to less than 8 and m is an integer from 1 up to the valence of R;

15

and the amine is selected from one or more compounds of the formulae

$(\text{H})_d-\text{Y}-(\text{R}^2-\text{M}-(\text{R}^2)_y)_b$ where

M is an amine or polyamine, linear, branched or cyclic, with at least one tertiary amine group;

20

R^2 at each occurrence is independently a moiety having 1 to 20 carbon atoms;

y is an integer from 0 to 6;

Y is oxygen or nitrogen; and

25

b and d are 1 when Y is oxygen and when Y is nitrogen, b and d are either 1 or 2 such that the sum of b and d is 3.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/018671

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 010 963 A (ERNER WILLIAM E) 28 November 1961 (1961-11-28) cited in the application example VII	1-13
X	US 4 040 992 A (BECHARA IBRAHIM S ET AL) 9 August 1977 (1977-08-09) cited in the application example 9 column 1, line 8 - line 11	1-13
X	US 5 539 007 A (LISTEMANN MARK L ET AL) 23 July 1996 (1996-07-23) cited in the application example 6 example 10 claim 1	1-13

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *G* document member of the same patent family

Date of the actual completion of the international search

13 October 2004

Date of mailing of the international search report

22/10/2004

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/018671

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 4 904 629 A (GALLA EDWARD A ET AL) 27 February 1990 (1990-02-27) example 6</p> <p style="text-align: center;">-----</p>	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/018671

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